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ANALYSIS OF MINERAL OIL BY SOLID-LIQUID ELUTION CHROMOTOGRAPHY

D. Stejaru, R. Popescu and N. Mosescu

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16. Abstract

A good separation of mono-, di-, tri-, and tetracyclic aromatic hydrocarbons was achieved by the method of adsorption chromatography on neutral alumina. The advantage of the method consists in the fact that in addition to the aromatic hydrocarbons mentioned, saturated hydrocarbons and resins can also be separated in a single operation.

The UV-monitoring of the eluted fractions showed that there was practically no mutual contamination of the hydrocarbon fractions. It is therefore sufficient to collect six fractions, which reduces the duration of the analysis considerably. The method as a whole is very simple and requires no special materials.

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ANALYSIS OF MINERAL OIL BY SOLID-LIQUID ELUTION CHROMOTOGRAPHY

D. Stejaru, R. Popescu and N. Mosescu

The composition of various petroleum products was determined largely by chromatographic methods. Adsorption chromatography with elution has permitted separation and determination of individual classes of hydrocarbons which are contained mainly in the heavy fractions of petroleum. /765*

Various procedures of separation are described in the specialized literature using silicon dioxide and aluminum oxides [1-7].

Most methods are based on combined separations; the first stage is the elution from silica gel, which permits separation into large classes of hydrocarbons (alkanes, aromatic compounds, heterocyclic compounds with nitrogen and oxygen), followed by a second stage of rechromatography of the aromatic hydrocarbons on aluminum oxide in order to separate and to determine the concentration of the hydrocarbons in relation to the number of rings in the molecule [1,2].

Some investigators used only aluminum oxide as the adsorbent for the integral separation of the individual classes of compounds which are contained in the heavy fractions of petroleum [3].

Different eluents are used in the separations by various methods. Generally, the following eluents were used: pentane,

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*Numbers in the margin indicate pagination in the foreign text.

benzene, ethyl ether, carbon tetrachloride, acetone, isooctanes, and alcohols [1-7].

With regard to characterizing the fractions obtained, this was currently done by means of the refraction index, density, molecular weight [7] as well as by spectral methods: UV absorption, mass spectrometry, nuclear magnetic resonance [3-6].

The present study contains the results of experiments performed in order to determine the individual classes of hydrocarbons in mineral oil, using elution chromotography as the method of separation and Al_2O_3 as the adsorbent.

Experimental results

The purpose of the study was to find an adsorbent which would allow us to obtain net separations of hydrocarbons with different numbers of aromatic rings in the molecule in order to determine as accurately as possible the chemical composition of the oils investigated and in order to shorten the time of analysis.

The elements were chosen in such a way as to obtain the shortest and most complete possible release of the components from the chromatographic column.

The experiment was carried out with three types of chromatographic adsorbents, i.e., neutral aluminum oxide, acid, and basic aluminum oxide.

All the adsorbents used had activity I, as established by the Brockmann method and were manufactured by E. Merck-Darmstadt.

The eluents used were: petroleum either (a mixture of equal amounts of n-pentane and i-pentane), benzene p.a. and

ethyl alcohol, p.a. The composition of the eluents in the sequence in which they were added to the column and the types of eluted hydrocarbons are presented in Table 1.

A total of 200 grams of aluminum oxide activated for 6 hours at 400°C were introduced and packed into the chromatographic column (Fig. 1). Subsequently, 15 grams of oil diluted with 15 ml of petroleum ether were added. When all the samples had penetrated the adsorbent, elution was started with petroleum ether (eluent 1) and the eluent was collected at the base of the column until the refraction index of petroleum ether was recorded. Elution was continued in the sequence illustrated in Table 1.

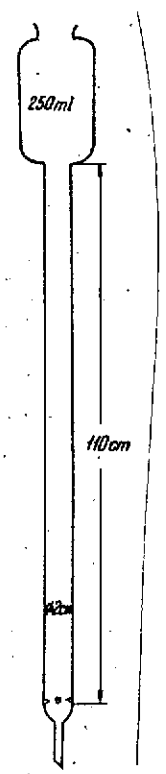

Fig. 1. Glass column used for chromatographic analysis of oils.

The fractions corresponding to each eluent were collected separately. Elution of each fraction was considered complete as soon as the pure eluent was liberated from the column. Quantitative determination of each fraction was made after complete removal of the eluent, by weighing and by measuring the refraction index using an Abbe refractometer, with an error of $\pm$ 0.0002.

The method permits precise determination of 6 types of hydrocarbons which are present in the fractions of petroleum investigated - saturated hydrocarbons, monocyclic, dicyclic, tricyclic and tetracyclic aromatic hydrocarbons and resins. The chromatograms obtained on three different types of alumina showed that under the conditions described, neutral alumina led to a clear separation of the components in the investigated oils (Fig. 2).

TABLE 1

ELUENTS USED FOR THE SEPARATION OF HYDROCARBONS FROM OILS ON ALUMINA

Number of the eluent	Composition of the eluent	Type of eluted hydrocarbon
1	petroleum ether	alkanes and cycloalkanes
2	5% benzene in petroleum ether	aromatic mononocyclic hydrocarbons
3	10% benzene in petroleum ether	aromatic dicyclic hydrocarbons
4	20% benzene in petroleum	aromatic tricyclic hydrocarbons
5	40% benzene in petroleum	
6	60% benzene in petroleum	
7	benzene	aromatic tetracyclic hydrocarbons
8	1% ethyl alcohol in benzen	aromatic polycyclic hydrocarbons
9	1:1 ethyl alcohol-benzene	heterocylcic compounds with S, O, and N.
10	ethyl alcohol	

When separation is done on different types of alumina and especially on the basic one, it was found that many fractions were contaminated with components of the neighboring classes of compounds, which led to different results (Table 2, Fig. 2, curves 2 and 3).

Table 3 contains data on the analysis of one of the oil samples investigated (medium distilled oil). The table shows that the large number of collected fractions as well

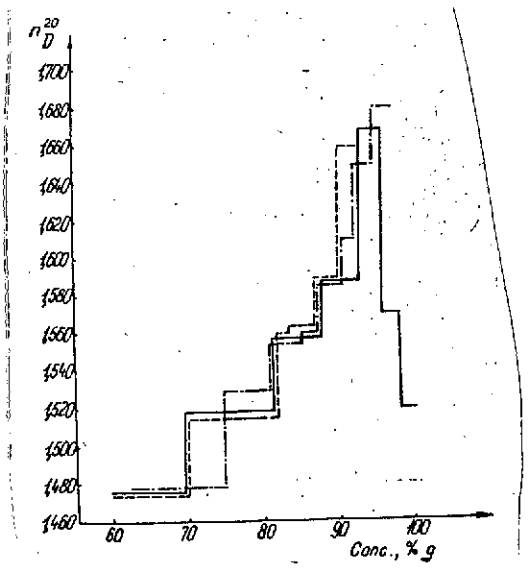

Fig. 2. Chromatograms obtained during analysis of a medium oil on three types of alumina: neutral alumina, acid alumina, basic alumina.

as the diversity of the eluents used, permitted separation even within the same group of compounds. This tendency towards separation within the same group of hydrocarbons is observed as a result of the variation in the refraction indexes of the fractions separated on neutral alumina. The phenomenon becomes more marked with the increase in the number of rings in the molecule.

The reproducibility of the method may be considered good. The variation of concentration within the same class of hydrocarbons in three different separations, does not exceed $\pm$ 0.5% in absolute value, as seen in Table 4. The yields obtained were better than 99%.

TABLE 2

COMPARISON OF THE RESULTS OBTAINED FROM THE ANALYSIS OF A MEDIUM DISTILLED OIL, USING THREE DIFFERENT ALUMINAS AS ADSORBENTS

Type of Hydrocarbon	Concentration in %g;		
	Neutral alumina	acid alumina	basic alumina
Alkanes and cycloalkanes	69,5	69.4	71.8
Aromatic monocyclic hydrocarbons	12,8	13,6	12.8
Aromatic dicyclic hydrocarbons	5,2	6,9	7,2
Aromatic tricyclic hydrocarbons	5,3	4,8	4,0
Aromatic tetracyclic hydrocarbons	0.9	—	—
Heterocylcic compounds with S, O and N	5,6	4,4	3,6
Losses	0,7	0.9	0,6

TABLE 3
ANALYSIS OF A MEDIUM DISTILLED OIL USING THREE DIFFERENT ALUMINAS AS ADSORBANT

Type of hydro-carbons	Concentration in %g	Neutral alumina % gr.	n_D^{20}
1	Acid alumina	69.30	1.4741
2	Aromatic monocyclic hydrocarbons	3.80	1.5111
3	Aromatic onocyclic hydrocarbons	9.1	1.5187
4	Aromatic dicyclic hydrocarbons	1.3	1.5558
5	Aromatic dicyclic hydrocarbons	2.0	1.5592
6	Aromatic dicyclic hydrocarbons	1.1	1.5651
7	Aromatic dicyclic hydrocarbons + 0.1% tricyclic	0.9	1.5715
8	Aromatic tricyclic hydrocarbons	2.3	1.5935
9	Aromatic tricyclic hydrocarbons	1.4	1.6170
10	Aromatic tricyclic hydrocarbons	1.0	1.6373
11	Aromatic tricyclic hydrocarons	0.6	1.6500
12	Aromatic tetracyclic hydrocarbons	0.6	1.6705
13	Aromatic polycyclic hydrocarbons	3.0	1.5688
14	Resins	2.5	1.5410
—	Losses	0.9	—

With regard to performing the analysis in series, the utilization of a smaller number of solvents than the one indicated in the tables is recommended. In order to shorten the time of analysis as much as possible, the solvents should be used only at the maximal concentration which is required in order to elute each class of hydrocarbons separately; thus, the number of fractions can be reduced to 6.

It shall be shown that the fractions separated with various solvents, as discussed in the article, should contain

TABLE 4

RESULTS OBTAINED AS A RESULT OF ANALYSIS OF A MEDIUM DISTILLED OIL SAMPLES ON THREE COLUMNS FILLED WITH NEUTRAL ALUMINA CONCENTRATIONS ARE EXPRESSED IN % WEIGHT

Type of Hydrocarbon	Determination		
	I	II	III
Benzene	69,5	70,0	69.4
Aromatic monocyclic hydrocarbons	12,8	12,6	12,3
Aromatic dicyclic hydrocarbons	5,2	5,5	5.3
Aromatic tricyclic hydrocarbons	5,3	5,1	5.4
Aromatic tetracyclic hydrocarbons	0.9	0.8	1,2
Resins	5,6	5,1	5,6
Losses	0,7	0,9	0,8

not only the hydrocarbons mentioned above, but also similar sulfur compounds; the sulfur compounds from local oils will be the subject of a future communication.

In order to establish the type of hydrocarbon and the purity of each fraction, the U.V. absorption spectra were recorded [6] using a Unicam model SP-800 spectrophotometer operating in the range of 200--400 nm.

As is known, the aromatic hydrocarbons grouped according to the number of rings have characteristic adsorption bands which can be used conveniently in this determination. In this case, the following absorption bands were used for characterizing the aromatic hydrocarbon groups: monocyclic 260-270 nm, dicyclic 270-290 nm, tricyclic 250-260 nm and tetracyclic 233-243 nm. The collected fractions were recorded after bringing them to a concentration ranging from 10^{-2} to 10^{-4}% in n-heptane. In addition, the extinctions were also measured in the ranges indicated, knowing that these grow by approximately one order of magnitude starting from the monocyclic and so on to the dicyclic compounds, etc. Working with 1 cm

cells in n-heptane, and determining the extinction coefficients, any impurities could be readily detected knowing that small amounts of dicyclic compounds which contaminate monocyclic ones increase considerably the absorption of the latter.

Conclusions:

Separation and determination of aromatic hydrocarbons, according to the number of the rings, is of interest, and therefore there have been frequent attempts to improve the existing methodology or to work out new methods of analysis. Thus, using neutral alumina as chromatographic adsorbent and a whole series of solvents, either pure or mixed in various proportions, we succeeded to achieve, in this study, a good separation of mono-, di-, tri- and tetracyclic aromatic hydrocarbons.

The advantage of this technique is that, in addition to the hydrocarbons mentioned, saturated hydrocarbons and resins can all be separated in a single operation.

Monitoring chromatographically separated fractions by means of U V absorption spectra showed that practically no contaminations were recorded in the different groups of hydrocarbons; this led to the conclusion that it is sufficient to collect 6 fractions, thus reducing the time of analysis and, the work volume on the whole, for performing this type of analysis. The whole method is particularly simple and requires no special materials.

BIBLIOGRAPHY

1. Mair, J.B., Marculaitis, W.J. Rossini, F.D., In: Anal. Chem., 29, 92 (1957).

2. Dornenburg, E. Serbolig, I., In: Brown-Boweri, 49/11-12, 590 (1962).

3. Snyder, L., In: Anal. Chem, 37/6, 713 (1965).

4. Mair, J.B., In: J. Chem. Eng. Data, 12/1, 126 (1967).

5. Snyder, L., In: Anal. Chem., 46/4, 774 (1964).

6. Pop, A., Teodorescu, V. Baciu, C., In: Petrol si Gaze, Supliment [Petroleum and Gases, Supplement] 19, 163 (1967).

7. Sergienko, S.R. In: